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(54) FLUORESCENT INK AND PREPARATION OF FLUORESCENT PRINT**(57)Abstract:**

PROBLEM TO BE SOLVED: To provide a fluorescent ink for ink jet printing which, even when it has a low viscosity suitable for high-speed ink jet printing, can yield a fluorescent print layer capable of emitting light at a high fluorescent intensity independently of the type (color and material) of a substrate and to provide a process for preparing a fluorescent print and a fluorescent print using the same.

SOLUTION: This fluorescent ink comprises a fluorescent dye and a vehicle, wherein the vehicle contains polyvinyl pyrrolidone. The polyvinyl pyrrolidone has a mol. wt. in the range of 5,000 to 150,000. The process for preparing a fluorescent print comprises printing the fluorescent ink by ink jet printing on a substrate. The fluorescent print comprises: a substrate; and a fluorescent print layer provided on the substrate, the fluorescent print layer comprising a fluorescent dye and polyvinyl pyrrolidone.

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[Claim(s)]

[Claim 1] Fluorescence ink for ink jet printing which is ink containing fluorescent dye and a vehicle, and is characterized by said vehicle containing a polyvinyl pyrrolidone.

[Claim 2] Fluorescence ink according to claim 1 ranges of whose molecular weight of said polyvinyl pyrrolidone are 5000-150000.

[Claim 3] Fluorescence ink according to claim 1 ranges of whose molecular weight of said polyvinyl pyrrolidone are 5000-15000.

[Claim 4] Fluorescence ink given in any 1 term of claims 1-3 which contain said polyvinyl pyrrolidone in 0.1 - 20% of the weight of an amount on the basis of weight of ink.

[Claim 5] Fluorescence ink given in any 1 term of claims 1-4 whose viscosity is the ranges of 1-10cPs.

[Claim 6] A manufacture method of a fluorescence print characterized by carrying out ink jet printing of the fluorescence ink given in any 1 term of claims 1-5 on a base material.

[Claim 7] A fluorescence print characterized by having a fluorescence printing layer containing fluorescent dye and a polyvinyl pyrrolidone on a base material.

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the manufacture method of the fluorescence ink for ink jet printing, and the fluorescence print by ink jet printing, and a fluorescence print. Furthermore, it is related with the manufacture method of a fluorescence print and fluorescence print using the fluorescence ink for ink jet printing which enables in detail fluorescence printing which may emit light by fluorescence intensity high irrespective of the color of a base material, and the viscosity of ink, and this fluorescence ink.

[0002]

[Description of the Prior Art] A fluorescence print has the fluorescence printing layer

which emits light by irradiating excitation light, such as ultraviolet rays, and will be in the condition which can be read. The print which a fluorescence printing layer cannot recognize substantially especially with the naked eye is useful as various information record means. For example, although it cannot usually recognize with the naked eye when a fluorescence printing layer is an invisible bar code, the information on a bar code can be read and checked if needed. Such an invisible bar code is effective as forged prevention means, such as for example, an instrument print, and a traffic coupon ticket, a commuter pass. Moreover, the fluorescence printing layer which cannot be recognized in naked eyes, such as an invisible bar code, is useful also as a means to record information required on it, without spoiling the appearance of a visible printing layer. For example, the information for retrieval can be given, without spoiling appearance by preparing an invisible printing layer in the front face of CD-ROM or LD.

[0003] In such a fluorescence print, in order to read information, it is required to be stabilized and to obtain the firefly luminescence reinforcement more than fixed. The case where a base material is colored, when a base material has a visible printing layer, and especially when, a part of fluorescence which emitted light is absorbed by the base material. Moreover, when a base material is transparency, a part of fluorescence which emitted light penetrates on the background of a base material. Therefore, high fluorescence intensity is especially needed in these cases.

[0004] By the way, to form such a fluorescence printing layer with an ink jet method is also tried. JP,54-22336,B -- ink jet printing -- service water -- sex ink is indicated. There is the method of making separate the minute drop of ink and forming a dot pattern in an ink jet method by applying electric field using ***** of the piezo-electric element by the pulse signal in the style of [of the method of forming a dot pattern by making ink breathe out from a nozzle, and the hypoviscosity containing the quality of electric field] high-speed ink. The former method can miniaturize a print speed, although it is late. On the other hand, the latter method is fit for the high-speed printing which used the large-sized machine.

[0005]

[Problem(s) to be Solved by the Invention] Generally the ink used for the ink jet method to which electric field are applied in the style of [above-mentioned] high-speed ink needs to be the hypoviscosity of the range of 1-10cPs. Moreover, the fluorescence printing layer formed by the ink jet method needs to have the firefly luminescence reinforcement which is a degree which can read information. It is possible to make it improve because the fluorescence intensity of a fluorescence printing layer increases the thickness of a fluorescence printing layer to it. However, in order to increase the thickness of a fluorescence printing layer, it is necessary to raise the viscosity of ink and

disagrees with needing hypoviscosity.

[0006] The fluorescence ink for ink jet printing currently indicated by said JP,54-22336,B is the hypoviscosity of the range of 1-10cPs. However, in this fluorescence ink, the luminescence reinforcement of a fluorescence printing layer was inadequate, and when especially a front face printed in a rude form, or when the background was coloring, the firefly luminescence reinforcement which is a degree which can read information was not obtained. It became impossible namely, to form the fluorescence printing layer which has the firefly luminescence reinforcement which is a degree which can read information until now by the ink jet method using the ink of hypoviscosity suitable for high-speed printing.

[0007] Then, even if the object of this invention is the case where it has the hypoviscosity suitable for high-speed ink jet printing, it is irrespective of the class (a color and construction material) of base material to offer the fluorescence ink for ink jet printing which can form the fluorescence printing layer which emits light by high fluorescence intensity. Furthermore, the object of this invention is to offer the manufacture method of a fluorescence print and fluorescence print which use the above-mentioned fluorescence ink for ink jet printing.

[0008] Wholeheartedly, as a result of research, this invention persons were using a polyvinyl pyrrolidone for the vehicle of ink, found out that the above-mentioned object was attained and completed this invention.

[0009]

[Means for Solving the Problem] This invention is ink containing fluorescent dye and a vehicle, and relates to fluorescence ink for ink jet printing characterized by said vehicle containing a polyvinyl pyrrolidone. Furthermore, this invention relates to a manufacture method of a fluorescence print characterized by carrying out ink jet printing of the fluorescence ink of above-mentioned this invention on a base material. Moreover, this invention relates to a fluorescence print characterized by having a fluorescence printing layer containing fluorescent dye and a polyvinyl pyrrolidone on a base material.

[0010]

[Embodiment of the Invention] Hereafter, this invention is further explained to details. The fluorescence ink of fluorescence ink this invention for ink jet printing contains a polyvinyl pyrrolidone as a vehicle. A polyvinyl pyrrolidone is polymer obtained by carrying out the radical polymerization of the N-vinyl-2-pyrrolidone. The thing of the type with which molecular weight is different is marketed, and it uses in some fields. the viewpoint of maintaining the viscosity of ink to below fixed, and raising fluorescence intensity in this invention to molecular weight -- 5000-150000 -- desirable --

5000-100000 -- it is more preferably suitable 5000-50000, and that it is the range of 5000-15000 still more preferably. In order to make viscosity of fluorescence ink into the value of fixed within the limits, it is necessary to lessen the content, so that the molecular weight of a polyvinyl pyrrolidone is large. In the case of the polyvinyl pyrrolidone of low molecular weight, the amount of coats of a polyvinyl pyrrolidone can be made [many], consequently high fluorescence intensity can be obtained.

[0011] Although the content of the polyvinyl pyrrolidone in the fluorescence ink of this invention is based also on the molecular weight of the polyvinyl pyrrolidone to be used, it is appropriate for it to consider as 5.0 - 15% of the weight of a range preferably 0.1 to 20% of the weight on the basis of the weight of fluorescence ink.

[0012] In addition to the polyvinyl pyrrolidone, the fluorescence ink of this invention may contain other resin as a vehicle. As such resin, for example Polyethylene system [polyethylene (PE), Ethylene-vinylacetate copolymer (EVA) and vinyl chloride vinyl acetate copolymer], A polypropylene (PP) vinyl system [polyvinyl chloride (PVC), a polyvinyl butyral (PVB), Polyvinyl alcohol (PVA), a polyvinylidene chloride (PVdC), Polyvinyl acetate (PVAc) and polyvinyl-formal (PVF)], Polystyrene system [polystyrene (PS), a styrene acrylonitrile copolymer (AS), ABS], acrylic [polymethylmethacrylate (PMMA), and MMA-styrene copolymer], A polycarbonate (PC), cellulose type [ethyl cellulose (EC), The cellulose acetate (CA) propyl (cellulose CP) acetic acid and a butanoic acid cellulose (CAB), Cellulose nitrate (CN)], fluorine system [poly chloro fluoro ethylene (PCTFE), A polytetrafluoroethylene (PTFE) and tetrafluoroethylene-hexafluoro ethylene copolymer (FEP), Poly vinylidene fluoride (PVdF)], an urethane system (PU), Thermoplastics, such as a nylon system [Type 6, Type 66, Type 610, and Type 11] and a polyester system [polyethylene terephthalate (PET), polybutylene terephthalate (PBT), and polycyclohexane terephthalate (PCT)], can be mentioned. The addition of these resin can be suitably determined in consideration of the luminescence reinforcement of the fluorescence printing layer formed.

[0013] In the light, colored or colorlessness is [that what is necessary is just the color which generates fluorescence] sufficient as the fluorescent dye contained in the fluorescence ink of this invention by irradiating excitation light. As colorless fluorescent dye, EB-501 (the Mitsui Toatsu Dye [Co., Ltd.] make, the luminescent color: blue), EG-302 (the Mitsui Toatsu Dye [Co., Ltd.] make, the luminescent color: yellowish green) and EG-307 (the Mitsui Toatsu Dye Co., Ltd. make --) Luminescent color : Green, ER-120 (the Mitsui Toatsu Dye [Co., Ltd.] make, the luminescent color: red), YUBITEKKU alumnus (the Ciba-Geigy make, the luminescent color: blue) called ER-122 (the Mitsui Toatsu Dye [Co., Ltd.] make, the luminescent color: red) and a

fluorescent brightener, an europium-thenoyltrifluoroacetone chelate (the product made from SHINROIHI, red lamp color), etc. can be mentioned.

[0014] Moreover, colored fluorescent dye can have the property which emits light in the same color as coloring, and can mention the cation brilliant flavin (yellow) of a basic dye, cation brilliant red (red), cation brilliant pink (peach), spa irone yellow (yellow), spa irone red (red), SOTTO pink (peach) (the Hodogaya chemistry company make), the BASIC yellow, Rhodamine B, etc. as the example.

[0015] The fluorescence ink of this invention may contain water and/or a water-soluble organic solvent further for the purpose of desiccation prevention, permeability grant, etc. of ink. The lower alcohol like the polyhydric-alcohol:N-alkyl pyrrolidone:ethyl acetate like :ethylene glycol which can mention the following as an example of a water-soluble organic solvent, a diethylene glycol, a polyethylene glycol, and a glycerol, the ester:methanol like amyl acetate, ethanol, propanol, and a butanol: It is glycol ether like the ethyleneoxide of a methanol, a butanol, and a phenol, or a propylene oxide addition product. These water-soluble organic solvents are not limited to the above-mentioned example of a solvent, and are suitably used by independent or plurality in consideration of the hygroscopicity of a solvent, moistness, color solubility and permeability, viscosity, the freezing point of ink, etc. The amount of these water-soluble organic solvents used can be 0.1 - 70% of the weight of a range on the basis of the weight of fluorescence ink.

[0016] In order to fulfill the terms and conditions furthermore required of the system of an ink jet recording device, it is also possible to add the additive known from the former as a component of ink if needed. As these additives, the alcoholic amines as a pH regulator, ammonium salt, the organic salt as a metal hydroxide:specific resistance regulator, the chelating agent as a mineral:anti-oxidant:antiseptics:antifungal agent:sequestering agent, etc. are mentioned. In order to consider as the ink suitable for high-speed printing, it is suitable for the viscosity of the fluorescence ink of this invention that it is the range of 1-6cPs preferably one to 10 cPs. The fluorescence ink of this invention mixes each above-mentioned component, and is manufactured by filtering if needed.

[0017] As a base material of a fluorescence print and the fluorescence print of the manufacture method this invention, they can be a form, a film made of resin, etc., for example. As a form, upper printing paper, middle-class printing paper, lower class printing paper, coat paper, light-weight-coat-paper, cast-coated paper (mirror coat paper), embossed-paper, art post, art paper, Japanese tissue printing paper, fine coating print sheet, brightening agent content paper, paraffin paper, impregnated paper, synthetic paper, fancy coated paper, and snow-white roll coat paper, color paper of fine quality, fluorescence paper, special print sheets (government postcard etc.), etc. can be

mentioned, for example. As a film made of resin, films made of resin, such as polyethylene, polypropylene, an ethylene-vinylacetate copolymer, polyethylene oxide, a polyvinyl chloride, a polyvinylidene chloride, polystyrene, a polyether, polyester, polyethylene terephthalate, nylon, cellulose acetate, ethyl cellulose, a cellulose nitrate, and a propyl cellulose, can be mentioned, for example. Colored printing may be performed to the base material.

[0018] The fluorescence ink of said this invention is printed on the above-mentioned base material. For example, the print which has a fluorescence printing layer can be manufactured by making the minute drop of ink separate and forming a dot pattern on a base material by applying electric field in the style of [which consists of fluorescence ink of this invention] high-speed ink.

[0019] Thus, in the fluorescence print of this invention obtained, it is appropriate for a polyvinyl pyrrolidone to contain in 80 - 99.9% of the weight of the range preferably 70 to 99.9% of the weight on the basis of the weight of a fluorescence printing layer. Moreover, the content to the fluorescence printing layer of fluorescent dye can be suitably determined in consideration of the luminescence reinforcement required of a fluorescence printing layer, the amount of a polyvinyl pyrrolidone, etc.

[0020]

[Example] Hereafter, this invention is further explained based on an example.

Example 1: Mix with the polyvinyl-pyrrolidone (eye ESUPI Japan K-15 and molecular weight 10000) 15.0 weight section, filter the europium complex ethanol solution (product made from SHINROIHI) 85.0 weight section which is a commercial fluorescent dye solution, and it is viscosity 5.5×0.5 cPs. Fluorescence ink was manufactured. Gravure coating of the above-mentioned fluorescence ink was carried out to paper of fine quality (90kg), and the fluorescence paint film with a thickness of about 0.01-0.05 micrometers was formed. In addition, about 0.01-0.05 micrometers in thickness are equivalent to the thickness of the printing layer formed by the ink jet method. The reinforcement of the fluorescence which used the fluorescence part optical altimeter (Shimazu RF- 5000) for this, irradiated excitation light with a wavelength of 350nm, and emitted light was measured. The luminescence peak was 611nm and luminescence reinforcement was 175.0. A result is shown in a table 1.

[0021] The example of a comparison: Ink was prepared according to the example 2 of JP,54-22336,B. Filtration purification of the constituent of pH9.6 which consists of the water-soluble acrylic resin solution [ethylene-glycol-monoethyl-ether [of methyl methacrylate, butyl acrylate, an acrylic acid, and the copolymer of 2-hydroxyethyl methacrylate] and solution (38% of nonvolatile matters) of ethanalamine] 6 section, the methanol 44 section, the europium-thenoyltrifluoroacetone chelate 0.5 section, the

distilled water 50 section, and the ammonium-chloride 0.2 section is carried out with a pore size 1.0micrometer membrane filter, and it is viscosity 5.5**0.5cPs. Fluorescence ink was manufactured. Except using the fluorescence ink manufactured by this, by the same method as an example 1, the fluorescence paint film with a thickness of about 0.01-0.05 micrometers was formed in paper of fine quality, and the luminescence reinforcement by 350nm excitation light was measured by the same method as an example 1. The luminescence peak was 611nm and luminescence reinforcement was 22.5. A result is shown in a table 1.

[0022]

[A table 1]

	ビヒクル	発光強度
実施例 1	ポリビニルピロリドン	1 7 5 . 0
比較例	アクリル樹脂	2 2 . 5

[0023] Examples 2 and 3: By the same method as an example 1, the fluorescence ink of the presentation shown in the following table 2 was manufactured. The viscosity of each fluorescence ink was adjusted to 5.5**0.5cPs.

[0024]

[A table 2]

	組成 (重量部)	
	実施例 2	実施例 3
ユーロピウムコンプレックスエタノール溶液*1	85.0	98.0
ポリビニルピロリドン (分子量10000) *2	15.0	—
ポリビニルピロリドン (分子量120000) *3	—	2.0

*1) Same fluorescent dye solution as what was used in the example 1 *2 The same polyvinyl pyrrolidone as what was used in the example 1 *3 K-eye ESUPI Japan 90, Molecular weight 120000 [0025] Gravure coating of the above-mentioned fluorescence

ink was respectively carried out to paper of fine quality (90kg), and the fluorescence paint film with a thickness of about 0.01-0.05 micrometers was formed. Moreover, gravure coating of the above-mentioned fluorescence ink was respectively carried out to color paper of fine quality (90kg), and the fluorescence paint film with a thickness of about 0.01-0.05 micrometers was formed. The reinforcement of the fluorescence which irradiated excitation light with a wavelength of 350nm and emitted light using the fluorescence part optical altimeter used for each fluorescence paint film obtained above in the example 1 was measured. The luminescence peak was 611nm. Luminescence reinforcement is shown in the following table 3.

[0026]

[A table 3]

	発光強度	
	上質紙	色上質紙
実施例 2	168.9	30.7
実施例 3	140.2	12.2

[0027] As a result of being the above, especially if it uses resin with small molecular weight in forming a fluorescence paint film in color paper of fine quality, it is clear that can make a fluorescence printing layer contain the polyvinyl pyrrolidone of more amounts, and higher fluorescence intensity is obtained.

[0028] Examples 4-6: By the same method as an example 1, the fluorescence ink of the presentation shown in the following table 4 was manufactured. The viscosity of each fluorescence ink was adjusted to 5.5**0.5cPs.

[0029]

[A table 4]

	組成 (重量部)		
	実施例 4	実施例 5	実施例 6
ユーロピウムコンプレックス	85.0	80.0	88.0
エタノール溶液*1			
ポリビニルピロリドン (分子量10000)*2	15.0	12.0	8.0
アクリル樹脂 *3	—	8.0	—
ブチラール樹脂 *4	—	—	4.0

*1) fluorescent dye solution *2 used in the example 1 Polyvinyl-pyrrolidone *3 used in the example 1 yes by the star photochemistry company -- loss X AW36H*4 Electrification butyral by electrochemistry company 2000L [0030] About the above-mentioned fluorescence ink, it is a transparent polyethylene film respectively. (thickness 188 mum) Gravure coating was carried out and the fluorescence paint film with a thickness of about 0.01-0.05 micrometers was formed. Paper of fine quality was hit against the rear face of each fluorescence paint film formation polyethylene film obtained above, and the reinforcement of the fluorescence which irradiated excitation light with a wavelength of 350nm and emitted light using the fluorescence part optical altimeter used in the example 1 was measured. The luminescence peak was 611nm. Luminescence reinforcement is shown in the following table 5.

[0031]

[A table 5]

	発光強度
実施例 4	34.8
実施例 5	50.0
実施例 6	57.3

[0032]

[Effect of the Invention] If ink jet printing is performed using the fluorescence ink of this invention, the fluorescence printing layer which emits light by high fluorescence intensity can be formed irrespective of the color of a base material. Consequently, the reading precision of the information printed in fluorescence ink improves. Moreover, since sufficient fluorescence intensity will be obtained even if a fluorescence printing layer is thin if the fluorescence ink of this invention is used, even when it prints with the ink jet method which uses the ink of hypoviscosity, high fluorescence intensity is obtained, and the reading precision of the printed information is high.